Broadening of Vibrational Raman Spectra by Concentration Fluctuations

A Molecular Dynamics Survey[1]

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ABSTRACT

Molecular dynamics calculations have been performed on model systems for nitrogen and mixtures of nitrogen with other compounds at high pressure, and at ambient temperatures. From these simulations the line shape of the Raman Q-branch was calculated. A short description of the applied methods are given. Our aim is to investigate whether line broadening, experimentally observed in mixtures, may be at least partially also invoked by critical fluctuations, as is suggested to be the case in nitrogen-helium mixtures. For this purpose it is necessary to investigate first the behavior of a non-critical mixture. We analyzed extensively the results of the mixture of nitrogen in neon at 2.4 GPa and 296 K, which is far away from a critical state. In this system a maximum in the linewidth is seen at equal volume fractions, experimentally as well as in simulations. The details revealed by the simulations allow a comparison with existing models, e.g. given by Knapp and Fischer. It is seen that assumptions made in that theory are in clear contradiction with the findings of the simulations.

KEY WORDS: computer simulations; linewidth, mixtures; nitrogen; Raman spectroscopy.

1. INTRODUCTION

During the last decade an increasing amount of information has been obtained about the vibrational spectra of simple fluids at high pressures by Raman spectroscopy. Especially, the Raman Q-branch of nitrogen has been chosen in many experimental investigations, either in pure substance [1,2] as well as in mixtures [2-6]. In the fluid phase of nitrogen at high pressures only one spectral line can be observed, which is characterized by its frequency (the "shift") and its shape, e.g. the linewidth, quantized by the "full-width at half maximum" (FWHM).

Nitrogen is also a favorable substance to study vibrational behavior at high pressures by means of computer simulations, in particular molecular dynamics (MD). First, the molecule is relatively simple, symmetric and has only one vibrational mode. At moderate temperatures, only a small fraction of the molecules is thermally exited (about 0.7% at room temperature). Further, since the rotational energy levels are very close, the rotations can be treated classically, i.e. continuously distributed at equilibrium. Moreover the vibrational population relaxation is very small and therefore the linewidth is determined mainly by dephasing. Finally, the internal energy as a function of the bond length as well as the intermolecular potential are well determined. The nitrogen molecule can be presented very well by a two-site model. Strictly speaking, one should determine simultaneously the vibrational motion of the sites as well as the trajectory of the molecule as a whole. In fact this is not possible. Due to the stiffness of the *intra*molecular force, time steps needed for the simulation of the vibrational motions are orders of magnitude less than those needed for the translations. On the other hand, this stiffness allows to treat the molecules as rigid rotors, which eases the calculations.

2. METHODS AND RESULTS

2.1 Pure nitrogen.

In a first approximation one can distinguish three causes for the deviation of the vibrational frequency of a molecule surrounded by other particles from that of an isolated, non-rotating molecule.

1)   Neighbor molecules exert forces with components along the axis of the vibrating molecule. As a result, the bond length changes. Because the atom-atom interaction is not purely harmonic, but includes also higher terms, the frequency changes continuously. This will be indicated below by the "first order external contribution" (E1).

2)   Because the external force will not be homogeneous the axial force will depend on the bond length. Thus, the first order derivative of the axial force to the bond length contributes to the harmonic constant of the vibrator: the "second order external contribution" (E2).

3)   Due to centrifugal forces the rotation of a molecule influences de bond length as well, and consequently vibration and rotation influence mutually: the vibration-rotation coupling (VR).

An effect that has been discarded as yet is the resonance transfer. The importance of this contribution is thought to be small in the fluid phase [7].

The relation between these momentary forces and the vibration frequency can be determined quantitatively using the well-known *intra*molecular energy function [8], which contains apart from a harmonic term also higher order coefficients. For purpose of our simulations, only the cubic term is significant.

In our first attempts [7], we simulated a system of nitrogen model particles in the fluid phase at 296 K and pressures from ± 0.07 GPa up to ± 2.4 GPa. Details of the simulations are given in refs. [7,9,10] but it is noted here that the model considered a

site-site potential between the atoms with a fixed interatomic distance. During each run the following topics have been surveyed.

1)   The mean value for the change of the vibration frequency $\langle\omega_{vib}\rangle$ i.e. the average over all particles and over all time steps of the sum of E1, E2 and VR.

2)   the width of the distribution of the momentary individual values of ω_{vib} by determining the standard deviation, usually called the "amplitude of modulation"

$$\Delta = \{\langle\omega^2_{vib}\rangle - \langle\omega_{vib}\rangle^2\}^{\frac{1}{2}} \tag{1}$$

3)   The time dependence of the momentary vibrational frequency, in terms of the normalized self-correlation function

$$\Omega(t) = \frac{\langle\omega(0)\omega(t)\rangle - \langle\omega(0)\rangle^2}{\Delta^2} \tag{2}$$

From this function, the correlation time τ_c was calculated

$$\tau_c = \int_0^\infty \Omega(t)\,dt \tag{3}$$

The addition of $\langle\omega_{vib}\rangle$ to the frequency ω_0 of a non-rotating, isolated molecule [8] gives the simulated shift. For the determination of the FWHM, use has been made of the theory given by Kubo [11]. In this theory, which will be quoted more extensively below, an expression is given for the linewidth under the condition that the frequencies are fast modulated, i.e. the system resides in the fast modulation regime

$$FWHM = 2\Delta^2\,\tau_c \; ; \tag{4}$$

$$\Delta.\tau_c << 1 \tag{5}$$

In Fig. 1 both experimental results [1,2] as well as results obtained by MD [7] are

displayed. A large discrepancy is clearly seen. Experimentally, an initial decrease of the
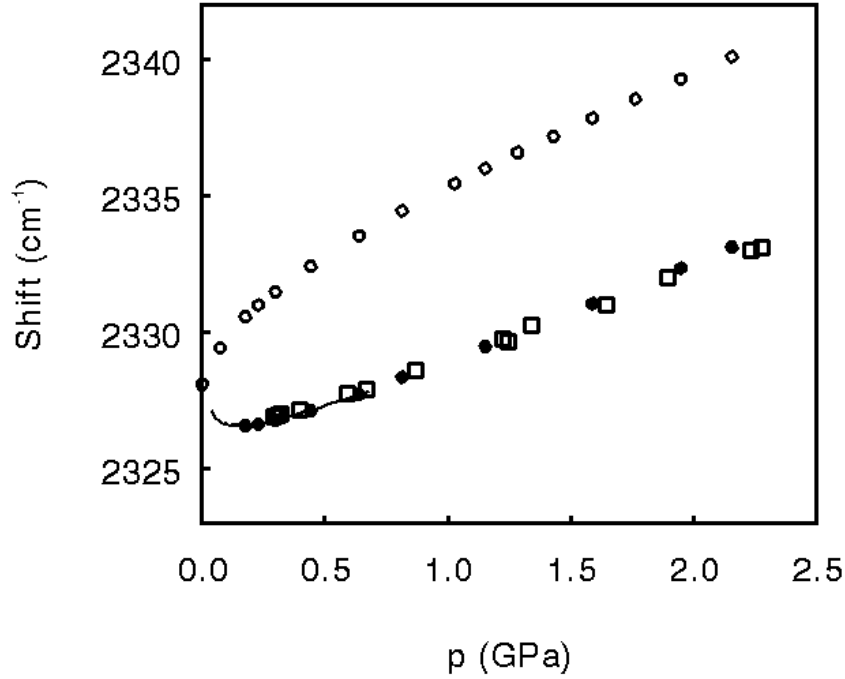
shift with

Fig. 1.

increasing pressure (red shift) is observed, followed by an increase above ca 0.2 GPa,

while the initially performed simulations always gave a blue shift. The most obvious

reason for this discrepancy is that the interaction of a particle with its surrounding

changes at excitation: an aspect neglected in our first approach. However, this energy

change is hard to determine theoretically. Therefore, we treated this problem in an

opposite way, and determined the jump in the dispersion energy from the difference

between the preliminary calculations and the experimental data. A suitable way was

found by adding a 12-6 Lennard-Jones potential (LJ), again as a site-site interaction

between the atoms. The strength of this potential ($\varepsilon/k_B = 0.3$ K; $\sigma = 2.95$ Å) is two

orders of magnitude less than the molecular interaction in the ground state, and therefore

regarded as negligible for the dynamics. It must be emphasized that also the repulsive

part of this LJ potential is necessary for a sound correction. Nevertheless, the choice for

this potential is -at least- traditional; the positioning at the atom sites is somewhat

arbitrary as well. It will be shown that this correction, indicated as the dispersion

correction (DC) plays a dominant role in the mechanisms of relaxation and line

broadening. Nevertheless, one must be aware of the fact that, due to the method applied,

the DC also includes the errors in experiments and simulations, e.g. the neglect of the

resonance transfer.

In the second stage of the calculations, the simulations have been repeated, now

with the addition of the DC as the fourth contribution to the shift, which obviously leads

to a sound correspondence with the experiments. The values for $\Delta.\tau_c$ range from 0.04 to

0.09. Thus, according to (5) the system may presumably be regarded to be in the fast

modulation regime and, consequently, the linewidth FWHM can be calculated with

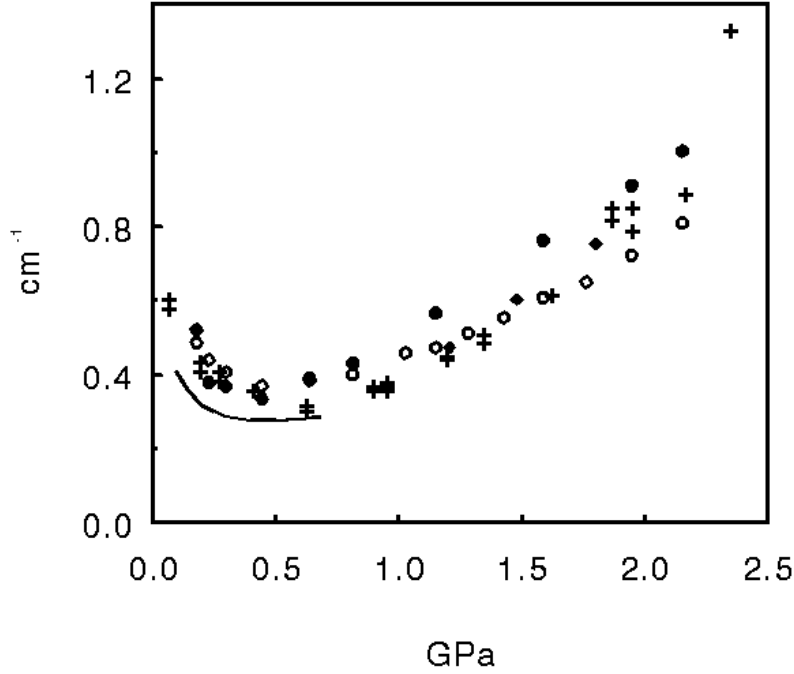formula (4). The results are pictured in Fig. 2. The addition of the DC increases the

Fig. 2.

linewidth at pressures above 1 GPa. Considering the experimental uncertainties, the

correspondence between experiment and simulation is rather good.

Computer simulations offer an unique possibility to reveal details generally

unobservable in the experiments. For instance, the various contributions to the

correlation function (2) can be determined. The vibration frequency ω_{vib} as a function of

time can be written as

$$\omega_{vib} = \omega_0 + \omega(t)$$

$$\omega(t) = \omega_{E1}(t) + \omega_{E2}(t) + \omega_{VR}(t) + \omega_{DC}(t) \tag{6}$$

with ω_0 the frequency of an isolated, non-rotating molecule.

Next the correlation function can be written as

$$\Omega(t) = \sum_{\alpha,\beta} \Omega_{\alpha,\beta}(t)$$

$$\Omega_{\alpha,\beta}(t) = \{\langle \omega_\alpha(0)\omega_\beta(t)\rangle - \langle \omega_\alpha(0)\rangle \langle \omega_\beta(0)\rangle\}/\Delta^2 \tag{7}$$

where α and β denote E1, E2, VR or DC, and Δ is again the total amplitude of

modulation (1)

From these functions the separate contributions to the correlation time can be calculated:

$$\tau_{\alpha,\beta} = \int_0^\infty \Omega_{\alpha,\beta}(t)\, dt$$

$$\tau_c = \sum_{\alpha,\beta} \tau_{\alpha,\beta} \tag{8}$$

In Fig. 3 the total autocorrelation function below 10 ps is pictured. The behavior shown

is qualitatively representative for all simulations on fluid nitrogen. Three regions can be

discerned: an initial rapid decrease, an interval with undulations, and finally a smooth
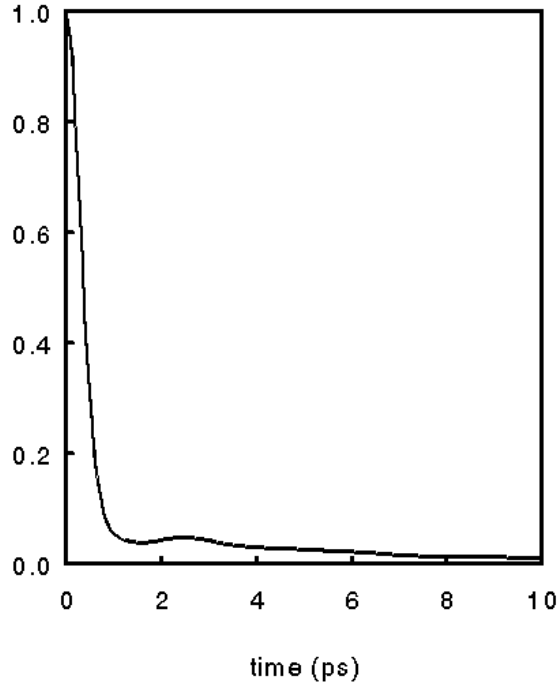
decay which approaches an

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Fig. 3.

exponential behavior. The complexity of the whole mechanism is demonstrated by Fig.

4, where all ten contributing functions, four diagonal and six cross terms, are drawn for

fluid N_2 just below the transition to the solid β phase. Note the importance of the cross-

correlations and the partial cancellations due to negative values of the cross-correlations

with the VR. Note as well that the latter, according to (1) and (7), do not contribute to

Δ^2, because in classical statistical physics, rotations and interactions are momentary

independent. Another consequence of the fact that all cross-correlations with VR are

negative is the occurrence of negative "correlation times" $\tau_{VR,\beta}$!
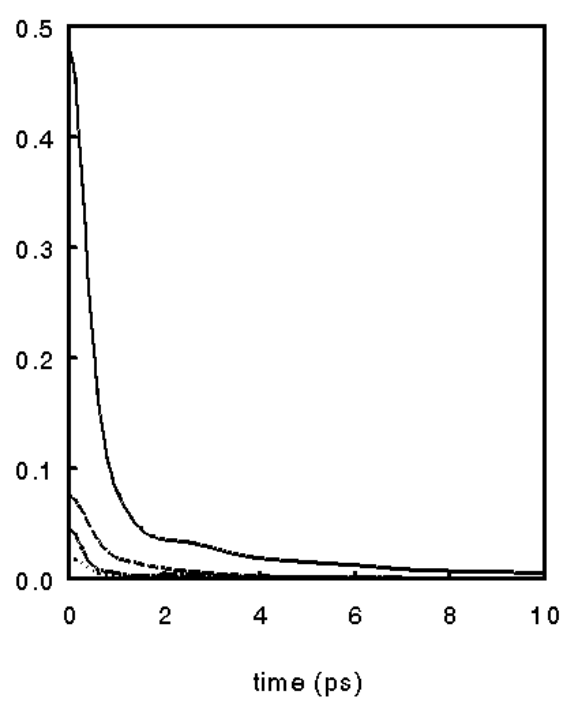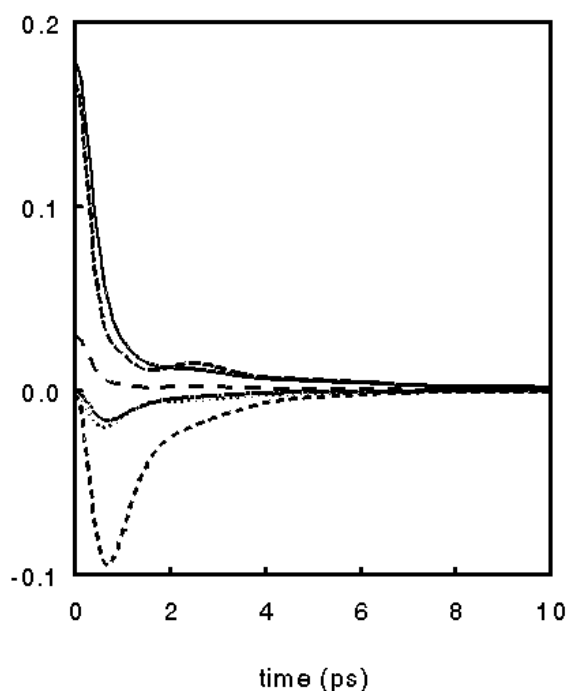
Fig. 4a.

Fig. 4b.

2.2 Nitrogen in mixtures.

Some years ago, results of high pressure Raman measurements of fluid nitrogen

in a mixture with helium have been published [3]. The investigators found a

considerable broadening at the critical composition which was attributed to critical

concentration fluctuations. They proposed that on the approach of the critical point, the

amplitude of these fluctuations increases and hence an inhomogeneous broadening was

achieved. In order to investigate this proposition, Kooi *et al.*[6] recently performed

similar experiments on mixtures of nitrogen with other compounds, e.g. neon. In

contrast with the He-N_2 mixture, the Ne-N_2 system has no critical demixing line at

ambient temperature. Nevertheless, again a clear line broadening was found, although

less than in the He-N_2 mixture. In order to reveal the underlying mechanisms and to

investigate to what extent critical behavior contributes to the broadening, MD simulations on model systems for both mixtures have been made. In this paper, we will discuss primarily the non-critical system Ne-N_2, which should be well understood before a critical behavior can be investigated.

It will be clear from the explanation given above, that for mixtures one needs, apart from the 'unlike' interaction with nitrogen in the ground state, a measure for the 'unlike' DC as well. Therefore, simulations have been performed at appropriate pressures and temperatures of one single molecule in a solvent. Similarly as for pure nitrogen, first a series of simulations had to be made without DC. The results for the frequency change with the pressure in various compounds, without DC, relative to the frequency of an isolated molecule are given in Fig. 5. Note that all results are close together and are about the same as for nitrogen in nitrogen and thus nearly independent of
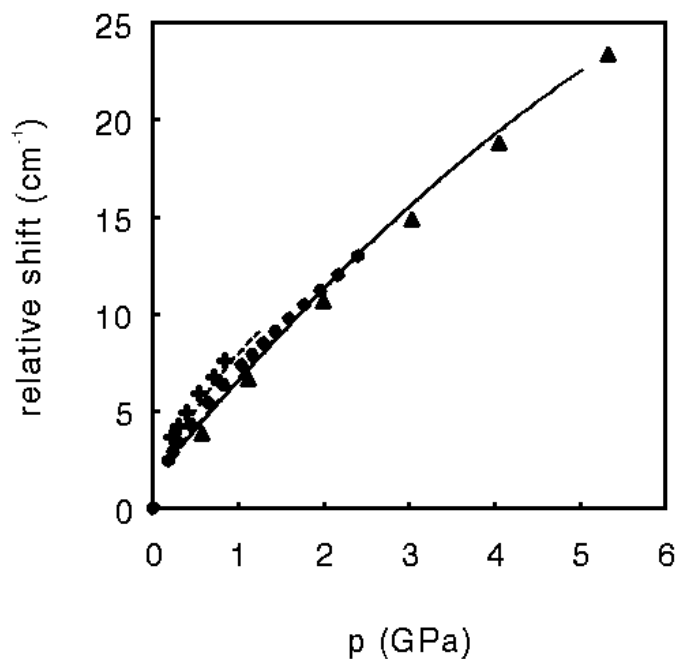
Fig. 5.

the intermolecular interaction. Experimental results for N_2 in He are slightly above these MD results, with neon as solvent slightly below, although always an increase with increasing density is seen ("blue shift"). Experiments with Ar [4] and Xe [5] show a clear red shift with a maximum of about 2.5 cm^{-1} and 4 cm^{-1} respectively. The increase of the DC with the mass of the solvent molecules reflects the higher polarizability of the large molecules: the different behavior in different solvents is mainly due to the DC. A most important conclusion is that, at a given pressure, the shift is primarily determined by the polarizability of the surrounding molecules and not by the intermolecular forces, acting on the nitrogen molecule.

Measurements on He-N_2 showed a maximum in the linewidth at a He mole fraction of $\pm$ 0.8, which corresponds to a volume fraction of $\pm$ 0.5. The measurements by

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Kooi *et al.* [6] have been performed on mixtures of N_2 with molar fractions Ne of 0.1, 0.65 and 0.95. In this mixture, the maximum linewidth was seen at a molar fraction of 0.65, corresponding again to volume fraction of $\pm$ 0.5. The broadening relative to the average of the linewidth of pure nitrogen and the infinite diluted nitrogen was about threefold in helium and twice in neon. It is mentioned above how the DC has been determined for N_2 in N_2 and for N_2 in He and in Ne. Assuming that the DC is binary additive, we simulated the vibrational behavior of nitrogen at several concentrations in these solvents, at 296 K and 2.4 GPa. Because the shift *without* DC hardly depends on the intermolecular potential, the concentration dependence of the shift is in fact only caused by the contribution of the DC. A remarkable feature is the linear dependence found for the DC, and thus for the shift itself, with the volume fraction. Even more remarkable is the observation that *also the amplitude of modulation does not deviate significantly from this linearity*. Problems arise with the determination of the correlation time. In the vicinity of a volume fraction of 0.5, the correlation function $\Omega(t)$ decreases too slowly to perform the numerical integration of formula (3), while the random scatter in the correlation function increases with time. This long persisting correlation is exclusively caused by the DC and its cross correlations. Only by extrapolations, approximate values for τ_c could be obtained, which are considerably larger than in pure nitrogen. As a consequence, the assumption of fast modulation (5) becomes questionable, and the linewidth may not be determined by Eq. (4). Therefore a more sophisticated method had to be adopted in these cases.

According to Kubo's theory the line shape $I(\omega)$ can be obtained as the Fourier transform of the relaxation function $\varphi(t)$

$$\varphi(t) = < \exp\{i\int_0^t dt' \omega(t')\} > \qquad (9)$$

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} \phi(t)dt \qquad (10)$$

It is obvious that the linewidth can be determined from Eq. (10), but even more interesting is the possibility to obtain the complete line shape. Near the fast modulation limit, the relaxation tends to a pure exponential and the line becomes Lorentzian, while in the limit of slow modulation, I(ω) reveals the momentary frequency distribution. Note that Kubo assumes in the explanation of his theory that the momentary distribution is gaussian, but only as a mathematical model. Only in that case his treatment leads to a gaussian limit in the slow modulation limit!

Very few calculations of the relaxation function obtained by MD with realistic potential models are known [12-15], and calculations of line shapes are even more scarce [14]. From our experience, it turns out that a straight forward application of this procedure leads to a line image which is seriously blurred by random noise. This is mainly caused by the increase of scatter in φ(t) at increasing t. It can be seen from the theory, that most information about the line shape is stored in the initial part of the relaxation function. At large times this function approaches an exponential. In our procedure, an exponential function was fitted for large values of t but the initial part was taken without smoothing. In Fig. 6 the experimental results for the FWHM in neon at
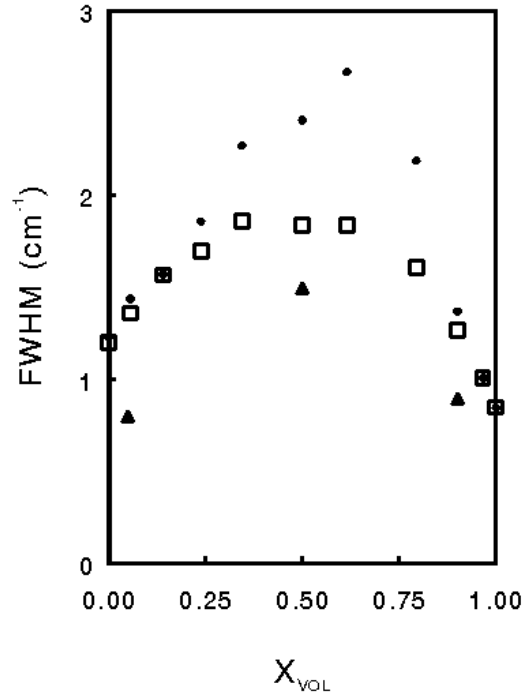
Fig. 6.

296 K and 2.4 GPa have been depicted, together with the results of the simulations.

First, the linewidth has been calculated as a function of the volume fraction, according

to Eq. (4), which assumes a fast modulation and a Lorentzian shape. The large scatter is

due to large uncertainties in the values for the correlation time, which in turn is caused

by the uncertainties in the extrapolations. Next, the linewidth has been calculated from

the Fourier transform of the relaxation function (10). For that purpose, an optimal fit

with a Voigt profile had been made using the Origin™ software package. It turned out

indeed that only at the extreme compositions, a Lorentzian fit suffices. Moreover, the

calculation of the linewidth using (4) leads to excessive values. The simulations allow

for a quantitative interpretation of the 'fast modulation criterion' (5) for this mixture.

We have shown elsewhere [10] that this criterion is not unambiguous, but depends on the system
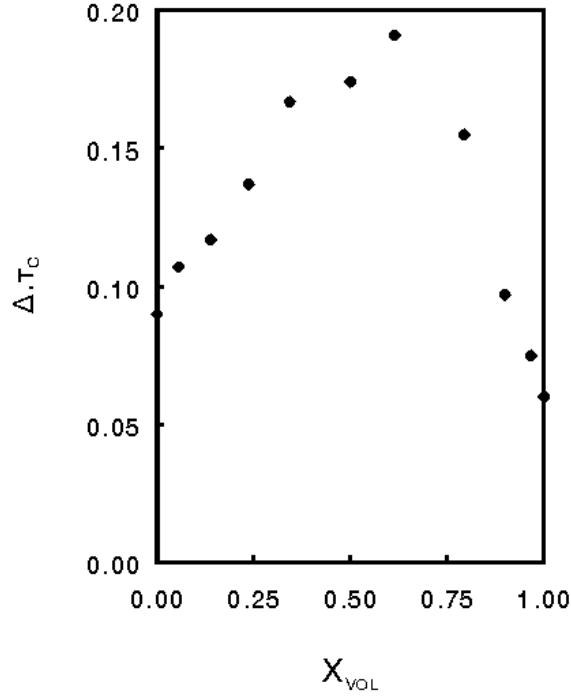

Fig. 7.

under consideration. From Fig. 6 and Fig. 7 it can be deduced that for values of $\Delta.\tau_c <$ *0.1* the criterion holds, but that already at slightly higher values, significant deviations occur, especially at high Ne content. Although a systematic discrepancy between the width of the Voigt profile and the experimental values is seen, the simulations describe the composition dependence properly. In Fig. 8 the change of the amplitude of modulation Δ is plotted as a function of the volume fraction of Ne. It is an important feature that the amplitude Δ changes only a few percent and does not reveal any significant deviation from a linear behavior. Also the change of the vibration frequency with respect to the frequency in the pure N_2 system is depicted in this plot.
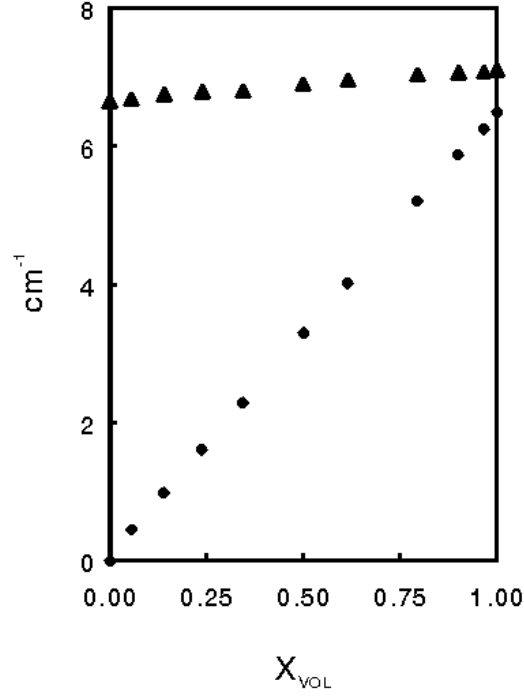
Fig. 8.

In table I some details are given for the three systems: pure N_2, 65% N_2 in Ne, and N_2 infinitely diluted in Ne, obtained by the simulations. It is seen that the contributions of $\Omega_{\alpha,\beta}(0)$ to $\Omega(0)$ and thus to Δ^2 change gradually from 100% N_2 to $\approx$ 0% N_2. No marked discrepancy is seen at 65%. In contrast, the contribution of the DC to the correlation time at this concentration is 17 times more than in the pure system and 80 times more than in the diluted system, although the initial value $\Omega_{DC,DC}$ is even less then in pure nitrogen. The reason is that the function $\Omega_{DC,DC}(t)$ decays very slowly in this mixture. As a result, the total value of τ_c is twice resp. threefold the value at the

extreme concentrations. In illustration, the correlation functions $\Omega(t)$ have been

depicted in Fig. 9 in a semi-logarithmic plot. It is seen that for pure nitrogen, values

above 30 ps are not significant. At infinite dilution, the correlation function becomes
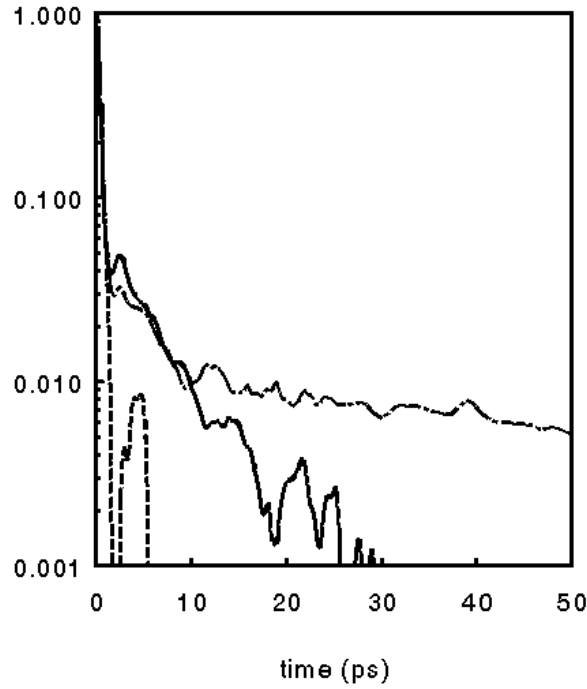
negative between 1.7

Fig. 9.

and 2.4 ps and is not significant above 8 ps. In the 65% mixture, the decay is even too

slow to determine the correlation time from direct numerical integration (3). An

estimate was made by an extrapolation using an exponential fit above 20 ps. Undoubted,

such extrapolations will increase the uncertainties in the results for τ_c. On the other

hand, a long persisting frequency autocorrelation function is accompanied by a fast

decaying relaxation function, for which an exponential fit at large times can easily be

made with only slight uncertainties. Consequently, also for this reason the method of the

determination of the linewidth from the relaxation function is the most suited in this situation.

3. DISCUSSION

Knapp and Fischer, [18] and Moser *et al*.[19] developed a theoretical approach of the problem of line broadening in mixtures. In short, they assume the existence of a few environmental states, formed by a discrete number of possible nearest neighbor molecules around the vibrating molecule. Each such state is assumed to cause a specific shift with finite width. Due to overlap of these frequencies, one broad line should be seen. This means that the line broadening is attributed to an increase of the amplitude of modulation. Further, it is argued that the influence of diffusion dynamics is small. The simulations discussed above lead to the opposite conclusion: the amplitude depends only very little on the interaction forces with the nearest neighbor molecules but depends on the difference of the polarizability of the solvent molecules, i.e. the DC. The result for the total amplitude turns out to be linear with the volume fraction of the solvent, without any exception at the concentration where the maximum in broadening is seen. Instead, a large increase in the correlation time, caused by the DC, has been found at those concentrations. The latter strongly indicates the importance of diffusion dynamics. In conclusion, even in systems far away from the critical state, a substantial line broadening is seen. The question then arises whether critical concentration fluctuations will give an extra contribution, as is supposed in ref.[2] for the system N_2 – He.

Generally, MD simulations are not considered very suitable for the study of critical behavior. In particular the systems are too small to enable large fluctuations. Nevertheless, if critical behavior is expected in virtually infinite systems, one may

expect that results of MD simulations should depend on the size of the sample systems. This dependency is the subject of a subsequent study. Simulations on several mixtures are in progress and reveal indeed marked results, which will be published in the near future.

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FIGURE CAPTIONS

Fig. 1. The shift of the Q-branch of N_2 at 296 K as a function of the pressure. Solid line and diamonds: experimental results [1,2] ; open circles and dots: MD results without DC and with DC. respectively [7].

Fig. 2. The linewidth (FWHM) for the N_2 Q-branch at 296 K as a function of the pressure.
Solid line and diamonds: experimental results [1,2]; crosses: experimental data from T_2 measurements [16,17]; open circles and dots: MD results without DC and with DC respectively [7].

Fig. 3. Autocorrelation function of the vibration frequency of N_2 at 296 K and 2.4 GPa.

Fig. 4. Contributions to the frequency autocorrelation function of N_2 at 296 K and 2.4 GPa.

a)   diagonal contributions: $\Omega_{\alpha,\alpha}(t)$. Top–down at t = 0: E1_E1; VR_VR; DC_DC; E2_E2.

b)   cross-correlations: $\Omega_{\alpha,\beta}(t) + \Omega_{\beta,\alpha}(t)$. Top-down at t = ± 0.5 ps: E1_E2; E1_DC; E2_DC; E2_VR; VR_DC; E1_VR.

Fig. 5. The shift of a single nitrogen molecule in an solvent relative to the frequency of an isolated (undisturbed) molecule, without DC, as a function of pressure.
Crosses: in Xe at 408 K. Further at 296 K: dashed line: in Ar; line: in Neon; triangles: in He; dots: N_2 in N_2.

Fig. 6. The linewidth at 296 K and 2.4 GPa. as a function of the volume fraction of Ne. Dots: calculated by $2\Delta^2\tau_c$; squares: by Fourier transformation of the relaxation function and Voigt fit; triangles: experimental.

Fig. 7. MD results for the Kubo factor $\Delta\tau_c$ for N_2 – Ne mixtures at 296 K and 2.4 GPa.

Fig. 8. MD results for the amplitude of modulation Δ: triangles, and the change in vibration frequency with respect to the frequency in pure N_2: dots.

Fig. 9. MD results for the frequency autocorrelation function at 296 K and 2.4 GPa. Solid line: pure N_2; dash-dotted line: 65% Ne; dotted line; N_2 infinitely diluted in Ne.

Table I. The amplitude of modulation, the correlation time, and the partial correlation functions of the vibration frequency and partial contributions to the correlation times in N_2-Ne mixtures at 296 K and 2.4 GPa.

α,β	0% Ne $\Delta =$ 6.63		65% Ne $\Delta =$ 6.92		$\approx$ 100% Ne $\Delta =$ 7.12	
	$\Omega_{\alpha,\beta}(0)$	$\tau_{\alpha,\beta}$ / ps	$\Omega_{\alpha,\beta}(0)$	$\tau_{\alpha,\beta}$ / ps	$\Omega_{\alpha,\beta}(0)$	$\tau_{\alpha,\beta}$ / ps
E1_E1	0.482	4.63	0.504	3.49	0.529	3.05
E2_E2	0.019	0.16	0.024	0.16	0.027	0.14
VR_VR	0.075	0.77	0.068	0.61	0.064	0.48
DC_DC	0.046	0.44	0.037	7.4	0.016	0.09
E1_E2	0.179	1.64	0.203	1.38	0.226	1.27
E1_VR	0	-1.45	0	-1.17	0	-1.00
E1_DC	0.169	1.47	0.137	1.23	0.114	0.61
E2_VR	0	-0.25	0	-0.21	0	-0.19
E2_DC	0.030	0.26	0.027	0.64	0.023	0.13
VR_DC	0	-0.33	0	-0.19	0	-0.11
total τ_C		7.36		13.3		4.53